Secondary Deuterium Isotope Effects in the Solvolysis of Cyclopropyl Triflates

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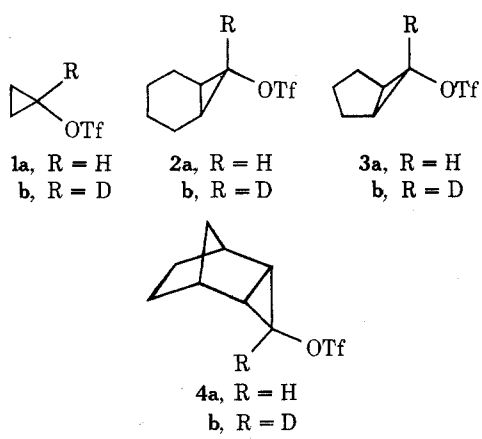
α-Deuterium isotope effects have been measured for solvolysis of cyclopropyl triflate (1), *exo*-bicyclo[4.1.0]hept-7-yl triflate (2), *exo*-bicyclo[3.1.0]hex-6-yl triflate (3), and *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-*exo*-3-yl triflate (4) in acetic acid. The respective values are 1.07, 1.08, 1.18, and 1.24. These values are discussed in terms of increasing cyclopropyl cationic character in the cationic intermediates. β-Deuterium isotope effects were determined for 1-methyl cyclopropyl triflate (8) and *endo*-6-methyl-*exo*-bicyclo[3.1.0]hex-6-yl triflate (9). Values were 1.12 and 1.42, respectively. The former value was considered to implicate a concerted ionization ring opening in 8. The latter value was consistent with a stepwise ionization, ring opening mechanism for 9. The β effect of 1.42 was considered small in view of the instability of the cation derived from 9 and rationalized in terms of an early transition state.

Secondary deuterium isotope effects have been used extensively in the study of solvolytic displacement reactions.[1] As tools for mechanistic diagnosis, they have proven to be quite useful. Our interest in cyclopropyl systems[2] has led us to use α and β secondary deuterium isotope effects as probes into mechanisms of solvolysis of cyclopropyl triflates. Previously, in a series of cyclopropyl triflates, rate responses to changing solvent ionizing power were quite small.[2b] In systems where neighboring group participation was possible, rate enhancements were also relatively small.[2] These results suggested an early transition state with little charge development. We have therefore introduced an α deuterium into a series of cyclopropyl triflates to see if such substitution could reveal any information as to the degree of charge development and distribution in the transition state for ionization of these systems. We have also measured the β effects in two tertiary cyclopropyl triflates. The results of these studies and their mechanistic implications are now reported.

α-Deuterium Isotope Effects. The α-deuterium isotope effect has been discussed extensively.[1,3] A value of around unity or slightly inverse is found for substrates solvolyzing by a purely nucleophilic mechanism. In contrast, compounds which solvolyze by "borderline" or limiting mechanisms show progressively increasing α-deuterium isotope effects. A maximum value of about 1.23 has been suggested by Shiner[3a] for the limiting solvolysis of a sulfonate ester. This value is a function of leaving group, being 1.125 for an alkyl bromide.[3a] The phenomenon of neighboring group participation will also result in a lowering of the α effects relative to the maximum value for a limiting solvolysis.[1,4] The α effect gives some measure of the hybridization changes and charge development in the transition state.

Deuterated triflates **1b–4b** were prepared to measure the α effect. The undeuterated triflates **1a–4a** had all been prepared previously.[2,5] The α-deuterated analogues were prepared by base-catalyzed exchange of the methyl ketones as shown in Scheme I. In general, exchange of the cyclopropyl proton was quite slow. These findings were in agreement with the previous observations of slow exchange of "activated" cyclopropyl protons.[6] In fact, the trideuterated ketone **6** could be isolated, uncontaminated with the tetradeuterated ketone, **7**. Additionally, treatment of *exo*-7-carbomethoxybicyclo[4.1.0]heptane with excess lithium diisopropylamide at −78 to 0 °C followed by quenching with deuterium oxide gave no deuterium incorporation in the recovered ester. Although the methyl ketones exchanged more rapidly than the corresponding methyl esters, in general, much more strenuous conditions were required for exchange of the cyclopropyl proton than the methyl protons. Cyclopropyl methyl ketone exchanged the ring proton faster than the corresponding bicyclic ketones. This implies a steric effect in which the fused ring system retards attack of base on the cyclopropyl proton. Conversion of the deuterated ketones to deuterated triflates **1b–4b** was accomplished as outlined in Scheme I.



Scheme I

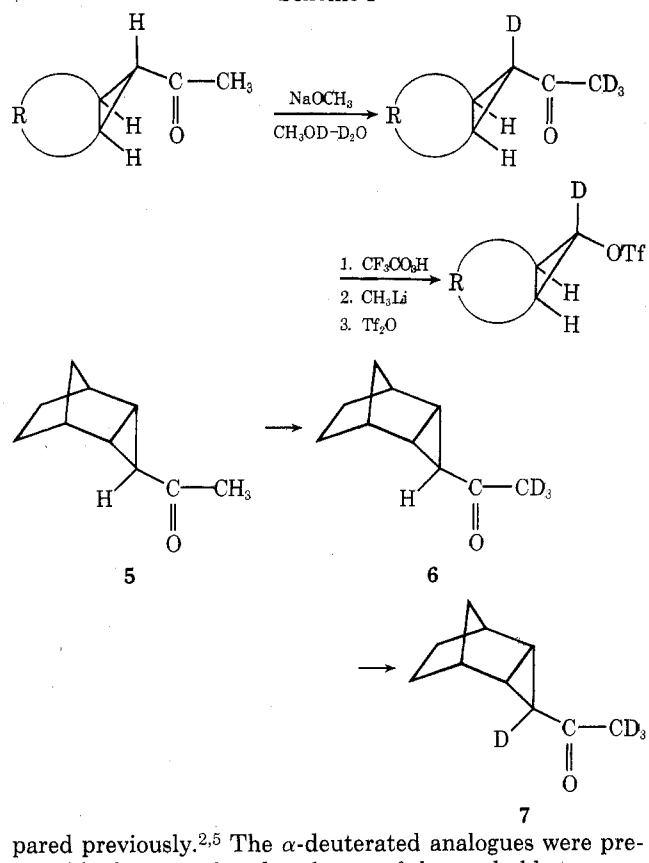


Table I. Rates of Solvolysis in Acetic Acid–0.1 M Sodium Acetate

Registry no.	Compd	Temp, °C	k, s^{-1}	k_H/k_D
25354-42-1	**1a**	90.0	$(1.24 \pm 0.00) \times 10^{-4}$	1.07 ± 0.01
60153-85-7	**1b**	90.0	$(1.16 \pm 0.01) \times 10^{-4}$	
60153-73-3	**2a**	80.0	$(7.61 \pm 0.05) \times 10^{-5}$	1.08 ± 0.01
60153-86-8	**2b**	80.0	$(7.05 \pm 0.02) \times 10^{-5}$	
25327-17-7	**3a**	150.0	$(2.85 \pm 0.04) \times 10^{-5}$	1.18 ± 0.02
60168-79-8	**3b**	150.0	$(2.41 \pm 0.01) \times 10^{-5}$	
56514-04-6	**4a**	140.0	$(4.30 \pm 0.03) \times 10^{-5}$	1.24 ± 0.01
60184-58-9	**4b**	140.0	$(3.47 \pm 0.01) \times 10^{-5}$	

Table II. Rates of Solvolysis in Acetic Acid–0.1 M Sodium Acetate

Registry no.	Compd	Temp, °C	k, s^{-1}	k_H/k_D
60153-74-4	**8a**	25.0	$(5.52 \pm 0.04) \times 10^{-5}$	1.12 ± 0.01
60153-87-9	**8b**	25.0	$(4.94 \pm 0.03) \times 10^{-5}$	
60153-71-1	**9a**	25.0	$(5.82 \pm 0.01) \times 10^{-5}$	1.42 ± 0.02
60153-88-0	**9b**	25.0	$(4.11 \pm 0.05) \times 10^{-5}$	

Table I gives α-deuterium isotope effects determined in acetic acid. The α effect appears to increase systematically as the degree of allylic cation character in the first cationic intermediate decreases. The relatively small value of the α effect (1.07) seen in cyclopropyl triflate (**1**) is in line with Schleyer's suggestion of an allylic cation as the first intermediate with transition state charge residing at all three positions.[5,7] Significant sigma assistance also accounts for the reduced α-deuterium isotope effect (1.08) seen in *exo*-bicyclo-[4.1.0]hept-7-yl triflate (**2**), in which a partially opened allylic cation has been proposed as the first intermediate.[8] The magnitude of the isotope effect implies that substantial charge resides at the allylic positions.

exo-Bicyclo[3.1.0]hex-6-yl triflate (**3**) is also suggested to give a partially opened allylic cation as the first cationic intermediate.[5,8b] However, because of strain in such a cation, internal cyclopropane bond fragmentation is minimal and charge should reside largely at the 6 position. This proposal is borne out by the increased α-deuterium isotope effect (1.18) seen in **3**.

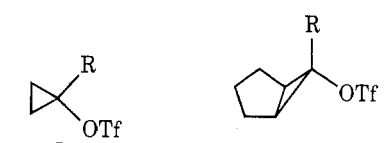
Triflate **4** has been suggested to undergo solvolysis to give a discrete cyclopropyl cationic intermediate with no opening of the internal cyclopropane bond.[2a] The observed α effect is 1.24. This value is in conformity with the value of 1.23 suggested by Shiner[3a] as maximum for a sulfonate ester. However, is this α effect to be expected in a solvolysis which gives a cyclopropyl cationic intermediate? Other evidence may indicate otherwise. Schiavelli[9] has measured the α-deuterium isotope effect for solvolysis of a bromoallene in which the hybridization change is $sp^2 \rightarrow sp$. The value of the α effect was 1.22, a value *larger than* the proposed maximum value of 1.125 for an $sp^3 \rightarrow sp^2$ hybridization change in the limiting solvolysis of alkyl bromides. This increased isotope effect was rationalized in terms of exchange equilibrium constants which predict a larger α effect for an $sp^2 \rightarrow sp$ hybridization change.

The bonding in cyclopropane has been discussed in terms of carbon $sp^{2.5}$ hybridization of the C–H bonds.[10] This accounts for, among other things, the increased acidity of cyclopropanes relative to less strained analogues. The overall hybridization change in ionization of triflate **4** should therefore be from $sp^{2.5} \rightarrow sp^{1.5}$. Although pertinent exchange equilibrium constants are not available, it would not be unreasonable to expect that the maximum α effect for this process should be between the maximum effect suggested by Shiner (1.23) and the maximum effect for an $sp^2 \rightarrow sp$ change (1.17×1.23).

As such the value of 1.24 observed for triflate **4** may be smaller than "normal" considering the hybridization changes involved. This could reflect the early transition state proposed for cyclopropyl triflates suggested on the basis of low response to solvent ionizing power.

β-Deuterium Isotope Effects. The β-deuterium isotope effect is thought to arise from a decreased C–D hyperconjugative interaction relative to C–H hyperconjugation.[3a] Attempts have been made to attribute this effect, as well as the α effect, to solely steric factors.[11] Shiner has pointed out the shortcomings of these suggestions[3a] and steric contributions to the β effect are considered only small factors.[12] Representative values for limiting solvolyses are 1.22 for α-phenethyl chloride[13] and 1.48 for 2-methyl-2-adamantyl chloride.[14] As with the α effect, neighboring group participation decreases the β effect.[15,20]

Deuterated triflates **8b** and **9b** were prepared by variations of known procedures.[16] Reaction of methylmagnesium iodide-d_3 with 1,3-dichloroacetone followed by ethylmagnesium bromide and ferric chloride gave 1-methyl-d_3-cyclopropanol,[17] which was converted to triflate **8b**. Triflate **9b** was prepared



8a, R = CH_3 **9a**, R = CH_3
b, R = CD_3 **b**, R = CD_3

via the bromomethyl-d_3 ketone, cyclopentadiene adduct[18] as shown in Scheme II. Separation of the isomers **10** and **11** was accomplished by distillation and conversion of bromo ketone **10** to acid **12** was analogous to ring contraction of the chloro ketone.[19] Conversion of **12** to triflate **9b** was straightforward.

Scheme II

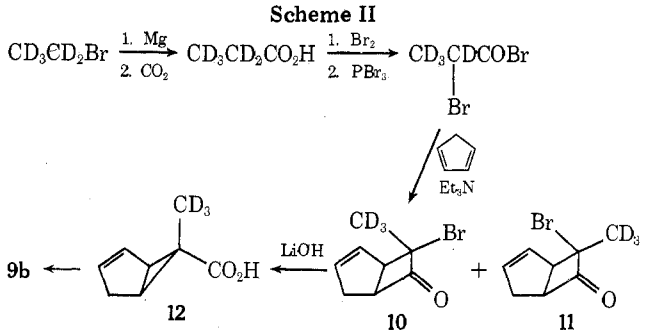
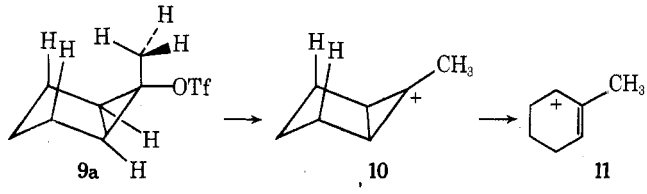


Table II gives β-deuterium isotope effects for solvolysis of triflates 8 and 9 in acetic acid. Previously, product and rate data did not allow assignment of a mechanistic pathway in the solvolysis of **8a**.[16] Only olefinic products were observed which could have arisen by stepwise or concerted processes. The magnitude of the β-deuterium isotope effect in the solvolysis of 8 is relatively small. This small value (1.12) supports a sigma assisted, concerted ionization, ring opening mechanism in preference to the formation of the 1-methylcyclopropyl cation as a discrete intermediate. Sigma assistance in 8 should be greatly reduced relative to the unsubstituted cyclopropyl system, **1**, even though allylic cations are the first intermediates produced in both cases. Apparently even a small amount of participation by the fragmenting cyclopropane bond gives a reduction in the β-deuterium isotope effect. The important feature is that the β effect of 1.12 is not consistent with a discrete cyclopropyl cationic intermediate.

Product studies have implicated the unopened 6-methylbicyclo[3.1.0]hex-6-yl cation (**10**) in the solvolysis of **9**.[16] The ring opened products obtained support a stepwise process in which the initially formed cation **10** rapidly opens to the 2-methylcyclohexenyl cation **11**. The measured β isotope effect



9a **10** **11**

is 1.42, a value significantly larger than the value for 1-methyl cyclopropyl triflate (**8**). A question arises concerning the normalcy of this value. We believe that this value is quite small in view of the system under consideration. Firstly, the unopened cyclopropyl cation, which is involved in the solvolysis of **9**, is quite unstable and hence should demand an unusually large amount of hyperconjugative stabilization. A standard system such as 2-methyl-2-adamantyl chloride, which gives a β effect of 1.48,[14] would not reflect the true demand of cation **10**. One of the largest β-deuterium isotope effects (1.86–2.33) has been observed in the solvolysis of 7-methyl-7-norbornyl tosylate.[14,20,21] This large value was presumed to result from the large demand for stabilization by the relatively unstable 7-norbornyl cation. More recently, Shiner and Sunko[14,22] have analyzed this effect in terms of α-methyl/α-hydrogen rate ratios. Their conclusion, in light of a "predicted" β isotope effect of 1.49, was that the measured isotope effect was unusually large and may be a result of partial rate determining elimination at an ion pair stage. Regardless of which value is a "normal" isotope effect in the 7-methylnorbornyl system, the demand for hyperconjugative stabilization in a cyclopropyl cation should certainly be larger than in the 2-adamantyl or the 7-norbornyl system.

Secondly, consider the relative solvolysis rates of **8a** and **9a**. Rates are approximately the same. The implication on the basis of the β effect is that the rate of **8a** is enhanced by σ participation. If this is true then **9a** must also be enhanced to account for the similarity in rate. Examination of molecular models suggests that steric factors are responsible for this rate enhancement in **9a**. Although steric factors are considered, in general, to contribute little to the β effect,[3a,12] we feel that a solvolytic steric isotope effect cannot be ruled out in very congested systems. That such effects can operate has been shown recently in solvolysis of 2-*tert*-butyl-2-adamantyl *p*-nitrobenzoate.[24] We can only speculate as to the magnitude of a steric isotope effect in **9**, but clearly it should complement the hyperconjugative effect.

Considering the demand for stabilization by the cyclopropyl cation **10**, and the possibility of an enhancing steric isotope effect, the measured β-deuterium isotope effect of 1.42 in triflate **9** must be considered quite small. Moreover, this value conforms to the implication[2b] that the solvolysis of cyclopropyl triflates leads to an early transition state. The β-deuterium isotope effect is not as large as one might naively expect since, in such a transition state, charge development is relatively small. Hence there is decreased demand for hyperconjugative stabilization relative to a later transition state, and a decreased β effect.

Experimental Section

Base-Catalyzed Exchange of Cyclopropyl Methyl Ketone. Cyclopropyl methyl ketone (Aldrich Chemical Co.) (3.0 g) was dissolved in 3 ml of methanol-d_1 and 10 ml of deuterium oxide containing 1.7 g of sodium methoxide. The mixture was refluxed for 40 h and extracted with two portions of pentane. The extracts were washed with a portion of water and solvents were removed by distillation through a glass helice packed column. The residue was distilled through a short-path condenser and the distillate was recycled under the same conditions. After an identical workup, the residue was isolated by distillation through a short-path condenser to give 0.781 g of tetradeuterated cyclopropyl methyl ketone. Mass spectral analysis showed complete exchange of the cyclopropyl proton.

Base-Catalyzed Exchange of Polycyclic Methyl Ketones. 7-Acetylbicyclo[4.1.0]heptane, 6-acetylbicyclo[3.1.0]hexane, and *exo*-3-acetyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**5**) were prepared by reaction of the corresponding carboxylic acids with methyllithium. The exchange reaction of ketone **5** was representative. A mixture of 0.68 g of ketone **5**, 0.17 g of sodium methoxide, 27 ml of methanol-d_1, and 20 ml of deuterium oxide was refluxed for 4 h. After an aqueous workup, 0.63 g of ketone **6** was isolated by distillation through a short-path condenser. Mass spectral and NMR data indicated no deuterium incorporation of the cyclopropyl proton and complete exchange of the methyl protons. Treatment of a 1.5-g sample of ketone **5** with 12 ml of deuterium oxide, 15 ml of methanol-d_1, and 2.6 g of sodium methoxide at 120–130 °C in sealed tubes for 10 h gave deuterated ketone **7**. Mass spectral data indicated complete exchange of the cyclopropyl proton. Infrared spectra of ketones **5**, **6**, and **7** show substantial differences.

Treatment of 1.55 g of *exo*-7-acetylbicyclo[4.1.0]heptane with 2 g of sodium methoxide in 20 ml of methanol-d_1 and 20 ml of deuterium oxide at reflux for 18 h gave complete exchange of the methyl protons but only about 50% exchange of the cyclopropyl proton. The ketone was recycled for 44.5 h at 100 °C in sealed tubes under the same conditions. Mass spectral analysis showed complete exchange of the cyclopropyl proton.

Treatment of 1.7 g of *exo*-/*endo*-6-acetylbicyclo[3.1.0]hexane with 2.4 g of sodium methoxide in 24 ml of methanol-d_1 and 22 ml of deuterium oxide for 18 h at reflux gave incomplete exchange of the cyclopropyl proton. Recycling at 100 °C for 42 h gave complete exchange.

Conversion of Cyclopropyl Methyl Ketones to Triflates. Conversion of deuterated methyl ketones to the corresponding acetates was accomplished by oxidation with peroxytrifluoroacetic acid in methylene chloride[25] using procedures analogous to oxidation of the protio analogues. Treatment of the acetates with methyllithium in ether followed by reaction of the resulting alcohol with trifluoromethanesulfonic anhydride in pyridine gave the triflate derivative. The following procedure was typical. A mixture of 1.0 g of *exo*-7-acetylbicyclo[4.1.0]heptane-d_4 and 13.8 g of dibasic potassium phosphate in 18 ml of methylene chloride was treated with peracid prepared from 0.52 g of 90% hydrogen peroxide and 4.87 g of trifluoroacetic anhydride in 5 ml of methylene chloride. The mixture was refluxed for 1 h and 45 min. After an aqueous workup, distillation gave 0.912 g (82%) of *exo*-7-acetoxybicyclo[4.1.0]heptane-d_4.

A solution of 0.8 g of acetate in 6 ml of ether was cleaved with 7 ml of 1.8 M methyllithium in ether. After cooling to −78 °C, water was added and the mixture was warmed to about 15 °C. The organic phase was separated, washed with water, and dried, and the solvent was removed by rotary evaporator. The crude alcohol was converted directly to triflate **2b** by treatment with a solution of 2.5 g of trifluoromethanesulfonic anhydride in 10 ml of pyridine at 0 °C. After 5 h at 0 °C, an aqueous workup gave 1.059 g (85%) of triflate **2b**, bp 58 °C (1.2 mm).

Preparation of 1-Methyl-d_3-cyclopropanol. The procedure was analogous to the procedure of DePuy[26] using methylmagnesium iodide-d_3 prepared from 10.0 g of methyl iodide-d_4 (Aldrich Chemical Co.; 99+ atom % D). The yield of product was 1.7 g (42%), bp 56–60 °C (80 mm).

Preparation of 2-Bromopropionyl Bromide-d_4. Ethyl bromide-d_5 (10.0 g) (Merck and Co., Inc., 99 atom % D) was converted to ethylmagnesium bromide-d_5 with 2.7 g of magnesium in 60 ml of ether. Carbonation by addition to excess carbon dioxide gave 4.64 g (68%) of propionic acid-d_5. Conversion to 2-bromopropionic acid-d_4 was accomplished by treatment with 10.0 g of bromine and 0.5 ml of phosphorus trichloride at 80–95 °C for 6 h. The crude bromo acid was treated with 15.9 g of phosphorus tribromide and the mixture was refluxed for 30 min. The crude product was distilled through a Vigreux column. After a small forerun of propionyl bromide, 16.2 g of a mixture of 2-bromopropionyl bromide-d_4 and an unknown impurity was obtained, bp 55–61 °C (16 mm).

Preparation of Bromo Ketones 10 and 11. The procedure was essentially that of Brady and Roe.[18] The 2-bromopropionyl bromide mixture obtained above in 30 ml of hexane was added over a 1.5-h period to a solution of 9.5 g of triethylamine in 65 ml of cyclopentadiene and 70 ml of hexane at room temperature. After filtration and an aqueous workup, the crude residue was distilled through a Vigreux column. The first fraction, bp 69.5–73 °C (1.3 mm), 1.69 g, was about 77% exo bromo ketone **10.** The second fraction, bp 73–80 °C (1.3 mm), 2.83 g, was about 70% endo bromo ketone **11.**

Preparation of *endo*-6-Methyl-d_3-*exo*-bicyclo[3.1.0]hex-2-enecarboxylic Acid (12). A 1.69-g sample of the bromo ketone mixture enriched in exo bromo ketone **10** was vigorously stirred for 2 h at room temperature with a solution of 1.13 g of lithium hydroxide in 11.5 ml of water. The solution was extracted with ether and the aqueous phase was added to a cold hydrochloric acid solution. The precipitate was collected and air dried giving 0.879 g (75%) of acid **12,** mp 65–70 °C. Conversion of **12** to triflate **9b** was completely analogous to the preparation of **9a.**[16]

Kinetic Procedure. The procedure was followed as previously described.[2a] For runs at 25 °C, the time was recorded when the end points of the titrations were reached. The rate constants reported represent the average of a minimum of two determinations.

Registry No.—5, 56552-97-7; **10,** 60153-89-1; **11,** 60208-18-6; **12,** 60184-59-0; trifluoromethanesulfonic anhydride, 358-23-6; 1-methyl-d_3-cyclopropanol, 60153-90-4; 2-bromopropionyl bromide-d_4, 60153-91-5; ethyl bromide-d_5, 3675-63-6; propionic acid-d_5, 60153-92-6; 2-bromopropionic acid-d_4, 60153-93-7; cyclopropyl methyl ketone, 765-43-5; 7-acetylbicyclo[4.1.0]heptene, 10330-36-6; *exo*-6-acetylbicyclo[3.1.0]hexane, 10330-37-7; *endo*-6-acetylbicyclo[3.1.0]-hexane, 60153-94-8.

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Thianaphthen-2-one Chemistry. 2. The Benzylidene Thiolactone Rearrangement: Synthesis of 2-Arylthianaphthene-3-carboxylic Acids and Esters

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The condensation of thianaphthen-2-one and aromatic aldehydes gave the corresponding 3-benzylidenethianaphthen-2-ones (**2**). Treatment of the benzylidene derivatives with ethanolic potassium hydroxide followed by acidification gave 2-aryl-2,3-dihydrothianaphthene-3-carboxylic acids (**3a–c**), while refluxing the benzylidene derivatives with methanol gave the methyl 2-aryl-2,3-dihydrothianaphthene-3-carboxylates (**3d, 3e**) (benzylidene thiolactone rearrangement). Oxidation of the dihydro acids and esters with DDQ (2,3-dichloro-5,6-dicyano-1,4-quinone) gave the corresponding 2-arylthianaphthene-3-carboxylic acids and esters (**4a–d**).

Earlier studies in these laboratories on the condensation of thianaphthen-2-one (**1**) with salicylaldehydes[1,2] led us to investigate the condensation of simple aryl aldehydes with **1** as a route to 3-benzylidenethianaphthen-2-ones (**2**). In the only prior report on such derivatives, Marschalk synthesized (Scheme I) 3-(2-methoxybenzylidene)thianaphthen-3-one (**2a**) which he claimed underwent hydrolytic scission to the mercaptostilbenecarboxylic acid (A) (Ar = o-$CH_3OC_6H_4$).[3] Having previously established the facile internal Michael addition of thiols to similarly activated double bonds,[1,2] we have reinvestigated Marschalk's claim and have found that the actual product is 2-(2-methoxyphenyl)-2,3-dihydrothianaphthene-3-carboxylic acid (**3a**).[4] This transformation of **2** to **3** resembles the well-known α-acyllactone rearrangement. However, there is no precedent for an α-benzylidenelactone undergoing this rearrangement, and other related α-exocyclic unsaturated lactones apparently experience only ring cleavage to hydroxy acid derivatives[5] (Scheme II). The enhanced nu-